Increasing the Energy Transfer Efficiency of DNA-Photonic Wires with Light-Harvesting Supramolecular Polymers

Mariusz Kownacki, S. M. Langenegger, R. Häner

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland
(mariusz.kownacki@dcb.unibe.ch)

Abstract: Photonic wires were constructed by sequentially arranging up to three fluorophores along a DNA scaffold with attached supramolecular phenanthrene polymers. These efficient light harvesting supramolecular polymers (SPs) are formed through the assembly of short DNA and non-DNA amphiphilic oligomers in water. This yielded SPs-DNA-modified photonic wires with the capacity to harvest and transfer excitation energy. Light - harvesting platforms efficiently drive Förster resonance energy transfer (FRET) through the DNA - photonic wires.

A $(Phe)_3$

B $(Phe)_5$ – GAAGGAACGTAGCCTGGAAC- 5‘

Complementary strands:

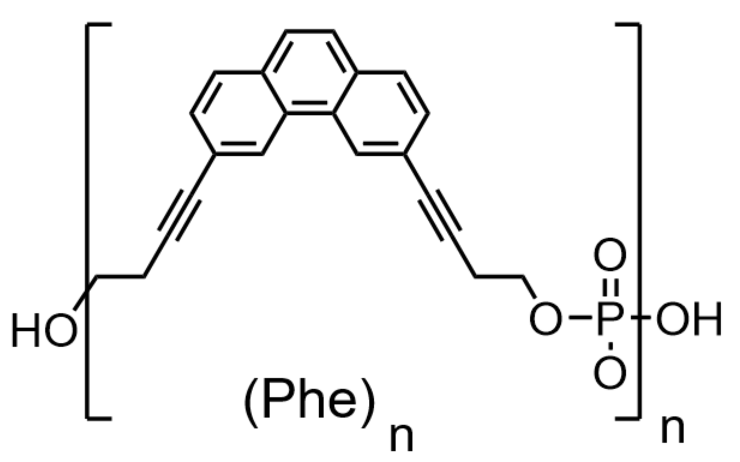
C Cy3 – CTTCCTTGCA - 3‘ – Cy5

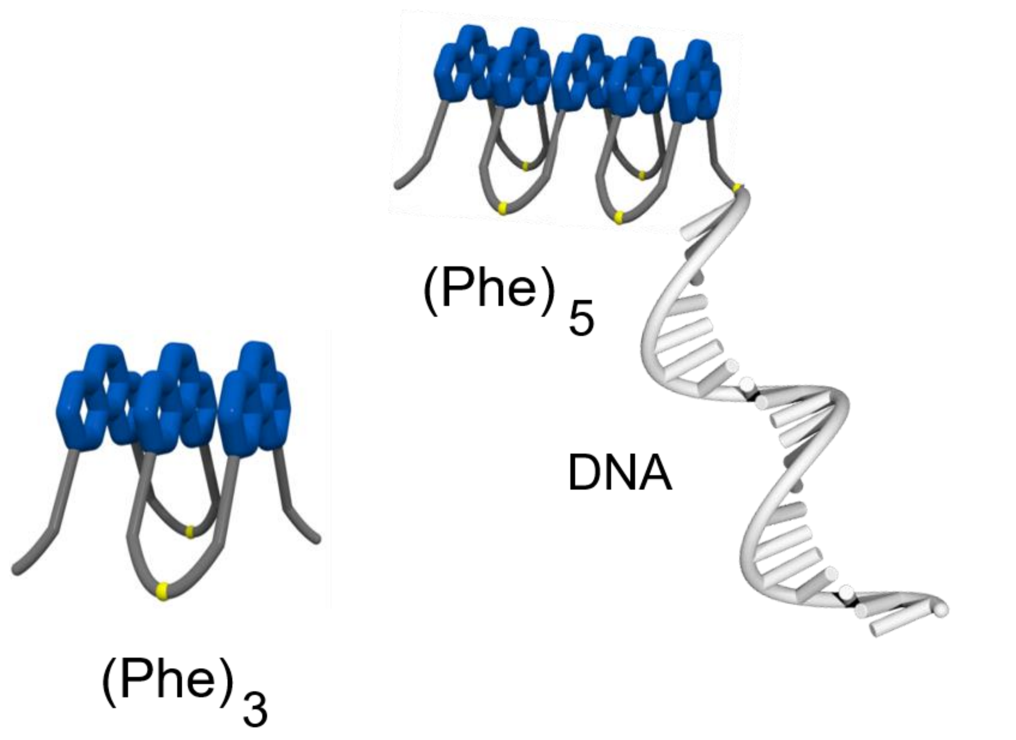
D TCGGACCTTG - 3‘ – Cy5,5

E CTTCCTTGCA - 3‘

F TCGGACCTTG - 3‘

G Cy3 – CTTCCTTGCA - 3‘





Scheme 1. Sequences of the modified oligonucleotides, chemical structure of phosphodiester – linked phenanthrene, and model representation of oligomers **A** and **B**: phenanthrene units (blue), DNA strand (gray), phosphodiester groups (yellow),

DNA-MODIFIED SUPRAMOLECULAR POLYMERS (SPs)

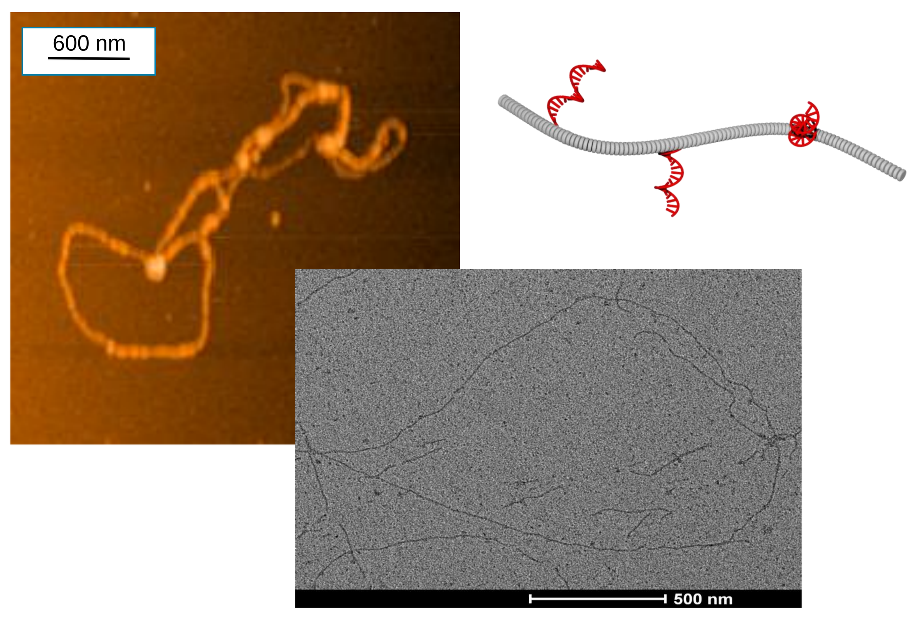
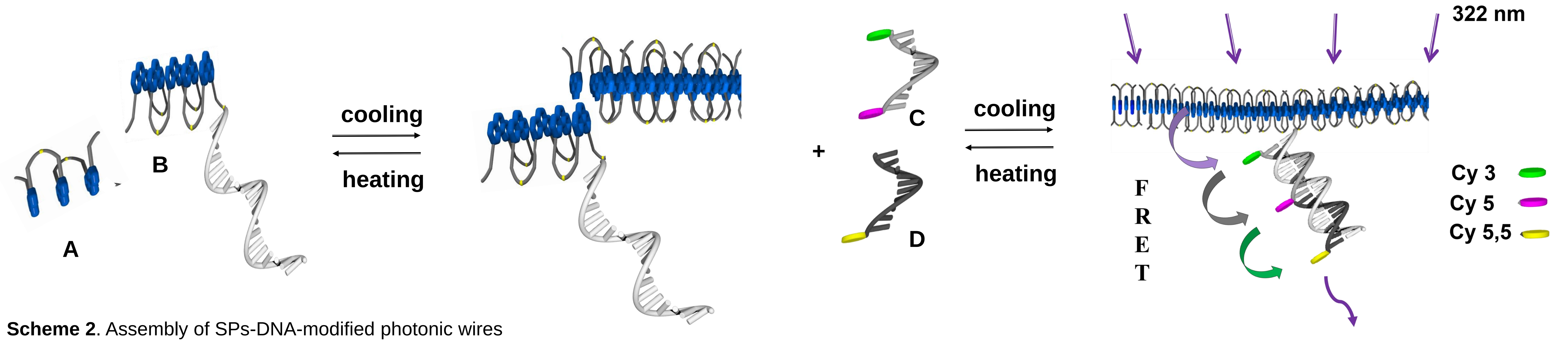


Figure 1. AFM and TEM images of DNA-modified supramolecular polymers formed from oligomer **A** and **B**. Conditions as in Figure 3.



Scheme 2. Assembly of SPs-DNA-modified photonic wires

SELF - ASSEMBLY

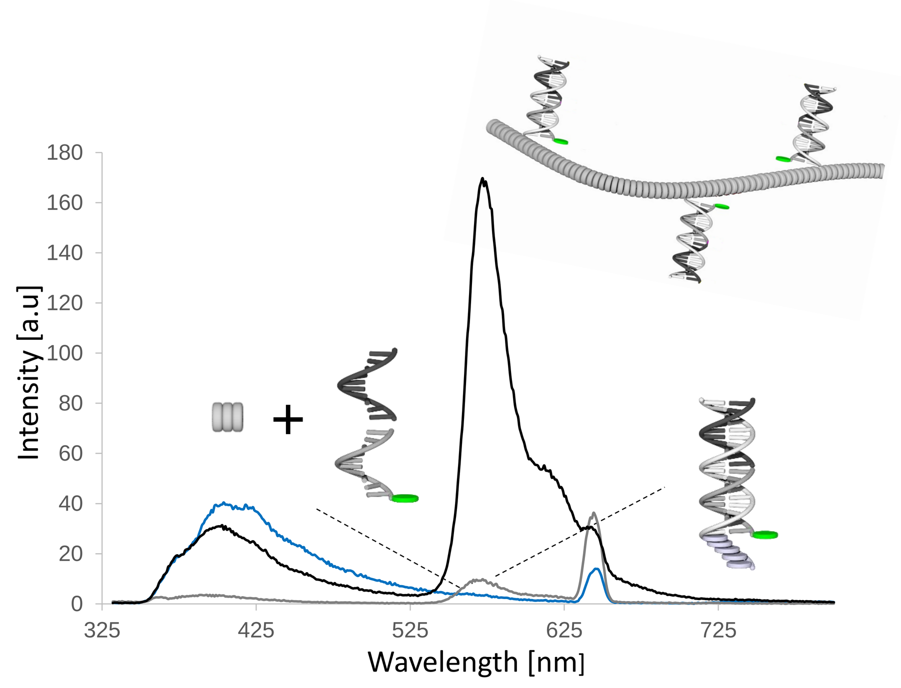


Figure 3. Fluorescence emission intensity of SPs–Cy3 (black) with comparison to oligomer A – Cy3 (blue) and oligomer B – Cy3 (gray). Concentrations: 0.5 µM of oligomer **A,** 0.015 µM of oligomer **B** (1.8 mol % DNA/Phe), 0.015 µM of oligomer **G** and oligomer **F** in 10 mM sodium phosphate buffer at pH 7.2 in the presence of 120 mM of NaCl.

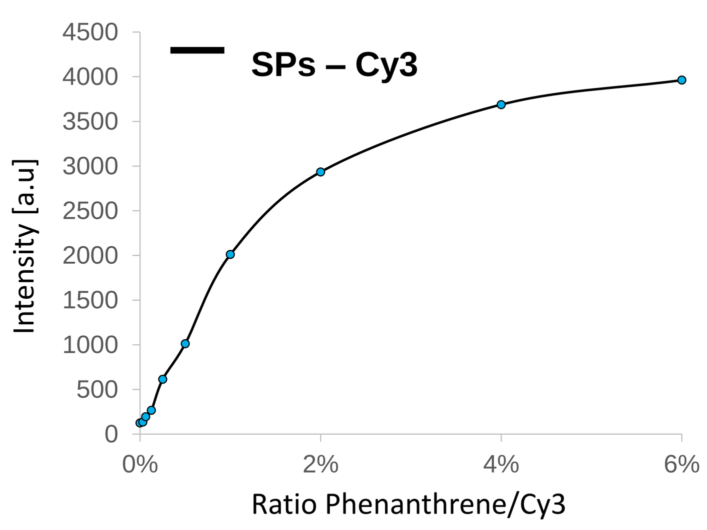


Figure 4. Dependence of the fluorescence intensity on the fraction of Cy3 as a function of phenanthrene / cyanine 3 ratio. Conditions as in Figure 3.

FÖRSTER RESONANCE ENERGY TRANSFER

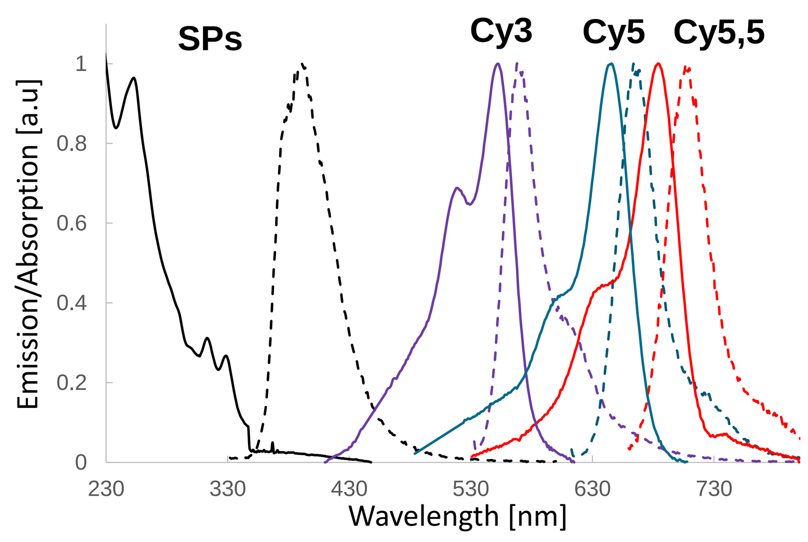


Figure 5. Normalized spectral overlap. Absorption (solid line) and emission (dotted line) spectra for DNA-modified SPs (black), Cy3 (green), Cy5 (blue) and Cy5,5 (red).

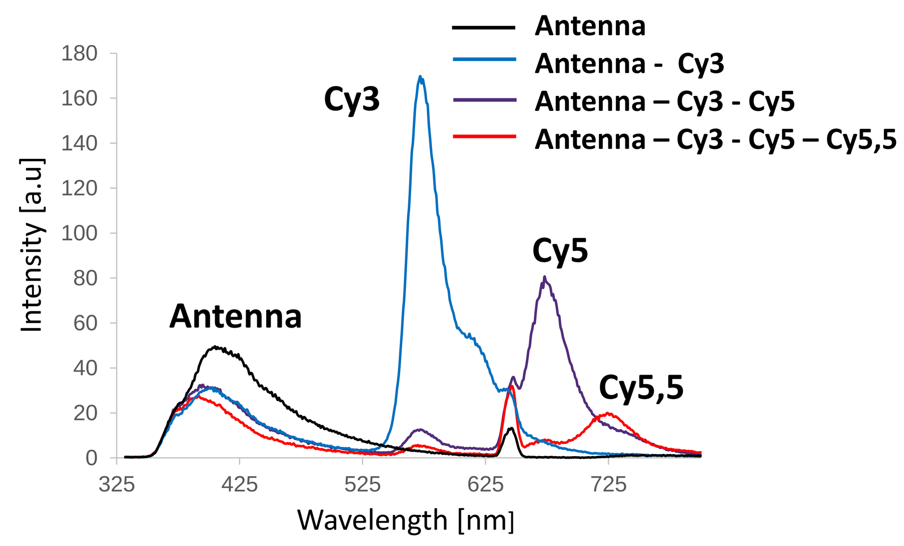


Figure 6. Fluorescence emission spectra of SPs-DNA-modified photonic wire upon phenanhtrene excitation (322nm) collected as sequential acceptor dyes on the DNA wire; placed consecutively from Cy3, through Cy5 to Cy5,5.

Coclusions: DNA-bioinspired supramolecular polymers (SPs) are forming promising light harvesting supramolecular platform. In these studies the SPs based platform was used to assemble extended photonic wire (SPs-DNA photonic wire). Energy transfer (ET) along the photonic wire through multiple, distinct fluorophores shows FRET mechanism. Photonic wire ET efficiency is increased with light harvesting supramolecular polymers with ability to funneling collected energy along the wire with emission in the near-infrared region

CASCADE ENERGY TRANSFER

CONFIGURATION	CY 3	CY 5	CY 5,5	
DONOR / ACCEPTOR POSITIONS:	Donor loss	Acceptor emission		Total energy emission
ANTENNA - CY3	100 %	-	-	100 %
ANTENNA - CY3 - CY5	7,4 %	48 %	-	55,8 %
ANTENNA - CY3 - CY5 - CY5,5	7.1 %	2,9 %	15,9 %	25,9 %

Figure 7. Table: estimated donor energy losses and acceptor emission efficiencies for self-assembled photonic wire polymers.

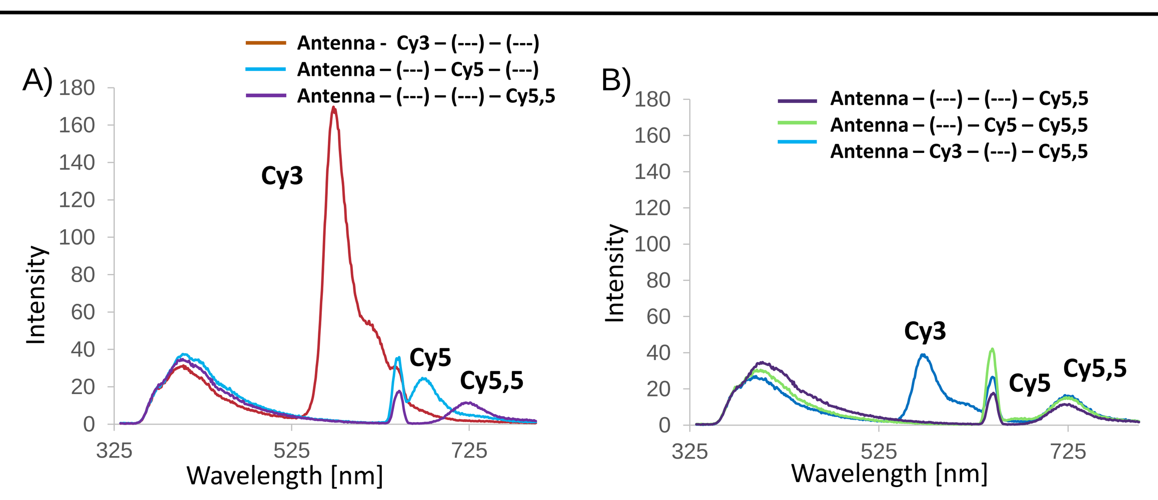


Figure 9. Fluorescence emission spectra of SPs-DNA-modified photonic wire; (A) All 3 dye-acceptors along DNA scaffold with their individual contributions (B) Cy5,5-DNA photonic wires in the absence/presence of one of the donor (Cy3 or Cy5).

Probst M., Langenegger S. M., Häner R., *Chem. Commun.*, 50, 159–161, **2014**
C. D. Bösch, S. M. Langenegger, R. Häner, *Angew. Chem. Int. Ed.*128.34: 10115-10118, **2016**
Dutta, P. K., Varghese R., Nangreave J., Lin S., Yan H., Liu Y. *J. Am. Chem. Soc.*, 133, p. 11985-11993, **2011**.

CONFIGURATION	CY 3	CY 5	CY 5,5	
Donor / Acceptor positions:	Donor loss	Acceptor emission		Total energy emission
Antenna - Cy3 - (---) - Cy5,5	23,3 %	-	12,5 %	35,8 %
Antenna - (---) - (---) - Cy5,5	-	-	9 %	9 %
Antenna - (---) - Cy5 - Cy5,5	-	2,1 %	11,8 %	13,9 %
Antenna - (---) - Cy5 - (---)	-	11,3 %	-	11,3 %
Oligomer B - Cy3	6 %	-	-	6 %
Oligomer B - Cy3 - Cy5	1,4 %	2,3 %	-	3,6 %
Oligomer B - Cy3 - Cy5 - Cy5,5	1,2 %	1,3 %	1,3 %	3,8 %
Oligomer B - (---) - (---) - Cy5,5	-	-	1 %	1 %

Figure 8. Table: estimated donor energy losses and acceptor emission efficiencies for different configurations of self-assembled photonic wire polymers.